OFFICE OF NAVAL RESEARCH

Contract N00014-84-K-0548

Task No. NR372-160

TECHNICAL REPORT NO. 13

Time-Independent Variational Approach to Inelastic Collisions of a Particle with a Harmonic Oscillator

by

Yasutami Takada

Department of Physics

University of California, Santa Barbara

Santa Barbara, CA 93106

Submitted for Publication

August 1988

OFFICE OF NAVAL RESEARCH

Contract N00014-84-K-0548

Task No. NR372-160

TECHNICAL REPORT NO. 13

Time-Independent Variational Approach to Inelastic Collisions of a Particle with a Harmonic Oscillator

by

Yasutami Takada

Submitted for publication

Department of Physics

University of California, Santa Barbara

Santa Barbara, CA 93106

ABSTRACT: A variational approach is applied to collisions of a particle having a mass m with a harmonic oscillator having a mass M in one dimension. We have used trial functions which become exact in the limit of either $m/M>>1$ or $m/M<<1$. We have derived exact expressions in the limit $m/M \rightarrow 0$ for inelastic as well as elastic collisions to leading order in the parameter m/M for any impenetrable interaction potential.

August 1988

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: TECHNICAL REPORT #13	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER: N00014-01	
4. TITLE (and Subtitle): TIME-INDEPENDENT VARIATIONAL APPROACH TO INELASTIC COLLISIONS OF A PARTICLE WITH A HARMONIC OSCILLATOR	5. TYPE OF REPORT & PERIOD COVERED: TECHNICAL REPORT 6/88 - 12/88
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): YASUTAMI TAKADA	8. CONTRACT OR GRANT NUMBER(s): N00014-84-K-0548
9. PERFORMING ORGANIZATION NAME AND ADDRESS: UNIVERSITY OF CALIFORNIA, PHYSICS DEPARTMENT, SANTA BARBARA, CA 93106, CONTRACTS & GRANTS, CHEADLE HALL, ROOM 3227	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: TASK NO. NR 372-160
11. CONTROLLING OFFICE NAME AND ADDRESS: OFFICE OF NAVAL RESEARCH, ELECTRONICS & SOLID STATE PHYSICS PROGRAM, 800 N. QUINCY, ARLINGTON, VA 22217	12. REPORT DATE: AUGUST 15, 1988
	13. NUMBER OF PAGES: -3-
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office): OFFICE OF NAVAL RESEARCH DETACHMENT, 1030 EAST GREEN STREET, PASADENA, CA 91106	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

"APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED"

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

REPORTS DISTRIBUTION LIST FOR ONR PHYSICS DIVISION OFFICE--UNCLASSIFIED CONTRACTS

18. SUPPLEMENTARY NOTES

(SUBMITTED FOR PUBLICATION)

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

collisions, harmonic oscillator

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A variational approach is applied to collisions of a particle having a mass m with a harmonic oscillator having a mass M in one dimension. We have used trial functions which become exact in the limit of either $m/M>>1$ or $m/M<<1$. We have derived exact expressions in the limit $m/M \to 0$ for inelastic as well as elastic collisions to leading order in the parameter m/M for any impenetrable interaction potential.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

S N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Time-Independent Variational Approach to Inelastic Collisions of a Particle with a Harmonic Oscillator

Yasutami Takada

Department of Physics, University of California
Santa Barbara
California 93106

and

*Institute for Solid State Physics**
University of Tokyo
Roppongi, Minato-ku
Tokyo 106, Japan

Abstract

A variational approach is applied to collisions of a particle having a mass m with a harmonic oscillator having a mass M in one dimension. We have used trial functions which become exact in the limit of either $m/M \gg 1$ or $m/M \ll 1$. We have derived exact expressions in the limit $m/M \to 0$ for inelastic as well as elastic collisions to leading order in the parameter m/M for any impenetrable interaction potential.

PACS 1987 numbers: 03.65.Nk, 34.50.Lf, 82.65.Nz 79.20.Rf

I. Introduction

Scattering of atoms from surfaces has received considerable attention in recent years.[1] Several theoretical methods have been developed to deal with this problem: The stochastic classical trajectory method,[2] the eikonal approximation,[3] the trajectory approximation,[4] and the semiclassical gaussian basis set method.[5] So far, however, fully quantum mechanical treatments are limited to theories[6-8] based on (first-order) distorted wave Born approximation (DWBA). In this paper, we propose another quantum mechanical treatment by employing a time-independent variational approach.[9]

Variational methods in scattering problems can be classified into three groups: The first one is based on the standard variational principles of Hulthén[10] and Kohn.[11] The second one is based on the Schwinger variational principle.[12] The last one is the combination of these two, first formulated by Takatsuka and Mckoy[13] for the phase shift and then by Gross and Runge[14] for the T-matrix. The advantage of this approach is that we can evaluate the T-matrix as easy as we can in the first approach without imposing the standard scattering boundary conditions on trial functions. For this reason, we will take the third approach.

In the present work, we consider a quantum-mechanical system, in one dimension, of a particle interacting with a fixed harmonic oscillator. This is a paradigmatic model and provides a ground for testing any approximate method to treat the problem of

atom-surface scatterings. The Hamiltonian of the system is

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2M}\frac{\partial^2}{\partial y^2} + \frac{M}{2}\omega^2 y^2 + V(x-y), \qquad (1)$$

where m and x are, respectively, the mass and coordinate of the incident particle ("incidon"), M, ω, and y are the mass, frequency, and coordinate of the oscillator respectively, and $V(x-y)$ is the mutual interaction which we assume impenetrable. When we measure energies and lengths in units of $\hbar\omega$ and $(\hbar/M\omega)^{1/2}$ respectively, the Hamiltonian (1) can be rewritten as

$$H = -\frac{1}{2\mu}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}y^2 + V(x-y), \qquad (1')$$

where μ is the mass ratio m/M.

In the past many workers treated this system. Secrest and Johnson[15] published a detailed numerical solution more than twenty years ago, mostly with an exponential repulsion between particles (the soft-core potential). Other approximate methods were also applied, for example, a purely classical treatment[16] which was developed later to the stochastic classical trajectory method, the method of Pechukas[17,18] which lead to the trajectory approximation, and first-order DWBA.[6] However, the most successful work was published by W.H. Miller[19] who dealt with general semiclassical collision theory including specific applications to the present model. For the collision parameters chosen by Miller, excellent agreement (to within a few percent)

with the numerical results was obtained by a simple semiclassical S-matrix treatment. The method of Heller[5] could also give as accurate results as Miller's method could.

The criterion for the validity of semiclassical calculation is that, for given initial oscillator and incident energies, the possible classical energy changes, ΔE_{cl} (which depend on the angle parameter of the oscillator), span several oscillator excitation quanta:

$$\Delta n = \Delta E_{cl}/\hbar\omega \gg 1. \qquad (2)$$

This is an expression of the correspondence principle. As is well known, suitable semiclassical calculations may give rather accurate results *even when the condition (2) is not satisfied*[20].

For given initial energies of the oscillator and incidon, the semiclassical condition (2) is *violated* in two regimes when, as is well known, classical energy transfer is small: (I) m>>M and (II) m<<M. The first regime is similar to the Born-Oppenheimer adiabatic regime for molecules, with the oscillator and incidon corresponding respectively to the molecular electrons and nuclei. The second regime may be called anti-adiabatic. We will treat primarily these two extreme situations in this paper.

In both regimes the collision is predominantly elastic. The inelastic collisions depend on the details of the potential $V(x-y)$ in the first regime, but they *do not* in the second one. Thus we can derive the exact expressions for inelastic collisions

to leading order in the parameter m/M. As will be shown in this paper, the results are the same qualitatively for all impenetrable potentials, but they differ quantitatively depending on whether $V(x-y)$ is (a) the step-function potential $V_0\theta(-x+y)$ with the Heaviside function $\theta(x)$, or (b) the hard-core potential $V_{HC}(x-y)$, defined by

$$V_{HC}(x-y) = \begin{cases} 0 & \text{for } x>y, \\ \infty & \text{for } x<y. \end{cases} \tag{3}$$

Results for any other impenetrable potential are reduced to those in one of these two cases. For example, the soft-core potential, $V_{sc}(x-y)$, given by

$$V_{sc}(x-y) = e^{-\alpha(x-y)}, \tag{4}$$

provides the same results as $V_{HC}(x-y)$. (A penetrable, localized potential gives qualitatively different results, but those results are the same as those for the delta potential $\lambda\delta(x-y)$, where λ is defined by

$$\lambda = \int_{-\infty}^{\infty} V(x)dx. \tag{5}$$

We will not consider this case in this paper.)

In Sec.II, we give a variational expression for reflection amplitudes and relate it with expressions in DWBA and the standard variational approach. We treat the adiabatic and anti-adiabatic

regimes in Secs.III and IV, respectively. Finally in Sec.V, we discuss some possibilities of improving on the results for the cases of $m \approx M$.

II. Variational Expression for Reflection Amplitudes

A. T-matrix

When we divide the Hamiltonian H into the unperturbed part H_0 and the interaction V, we can write the Lippman-Schwinger equation for the exact wave function $|\bar{\varphi}_i^{(+)}\rangle$ with outgoing wave boundary conditions as follows:

$$|\bar{\varphi}_i^{(+)}\rangle = |\varphi_{0i}\rangle + G_0^{(+)} V |\bar{\varphi}_i^{(+)}\rangle, \tag{6}$$

where $|\varphi_{0i}\rangle$ is the normalized eigen function of H_0 and $G_0^{(+)}$ is the Green's function, defined by

$$G_0^{(+)} = \lim_{\varepsilon \to 0^+} \frac{1}{E - H_0 + i\varepsilon}. \tag{7}$$

Quite similarly, the exact wave function $\langle\bar{\varphi}_f^{(-)}|$ with incoming wave boundary conditions satisfies the following equation:

$$\langle\varphi_f^{(-)}| = \langle\varphi_{0f}| + \langle\bar{\varphi}_f^{(-)}| V G_0^{(-)}. \tag{8}$$

As shown by Gross and Runge[14], the functional $[T]_{fi}$, introduced by

$$[T]_{fi} = \langle\varphi_{0f}|V|\varphi_{0i}\rangle + \langle\varphi_{0f}|VG_0^{(+)}V|\bar{\varphi}_i^{(+)}\rangle$$

$$+ \langle\tilde{\varphi}_f^{(-)}|VG_0^{(+)}V|\varphi_{0i}\rangle$$

$$- \langle\tilde{\varphi}_f^{(+)}|VG_0^{(+)}V - VG_0^{(+)}VG_0^{(+)}V|\tilde{\varphi}_i^{(+)}\rangle, \qquad (9)$$

is reduced to the exact T-matrix element $\langle\varphi_{0f}|V|\bar{\varphi}_i^{(+)}\rangle$, when trial functions $|\tilde{\varphi}_i^{(+)}\rangle$ and $\langle\tilde{\varphi}_f^{(-)}|$ are equal to the exact wave functions $|\bar{\varphi}_i^{(+)}\rangle$ and $\langle\bar{\varphi}_f^{(-)}|$, respectively. In addition, $[T]_{fi}$ is stationary for small variations of trial functions around the exact wave functions. Therefore Eq.(9) gives a variational expression for the T-matrix.

When we define $|\varphi_i^{(+)}\rangle$ and $\langle\varphi_f^{(-)}|$ by

$$|\varphi_i^{(+)}\rangle = |\varphi_{0i}\rangle + G_0^{(+)}V|\tilde{\varphi}_i^{(+)}\rangle, \qquad (10a)$$

and

$$\langle\varphi_f^{(-)}| = \langle\varphi_{0f}| + \langle\tilde{\varphi}_f^{(-)}|VG_0^{(+)}, \qquad (10b)$$

Eq.(9) can be rewritten in terms of $|\varphi_i^{(+)}\rangle$ and $\langle\varphi_f^{(-)}|$ as

$$[T]_{fi} = \langle\varphi_f^{(-)}|H-E|\varphi_i^{(+)}\rangle - \langle\varphi_{0f}|H_0-E|\varphi_i^{(+)}\rangle. \qquad (11)$$

Although trial functions $|\varphi_i^{(+)}\rangle$ and $\langle\varphi_f^{(-)}|$ are not required to satisfy the standard scattering boundary conditions, the incoming (outgoing) part of $|\varphi_i^{(+)}\rangle$ ($\langle\varphi_f^{(-)}|$) should be equal to $|\varphi_{0i}\rangle$ ($\langle\varphi_{0f}|$). This is the only requirement for trial functions in Eq.(11).

B. DWBA

If we know exact solutions of H_0+V_1 where V_1 is some interaction potential appropriate to the problem, we can rewrite Eq.(11) with the use of the exact solutions of H_0+V_1, $\langle\bar{\varphi}_{1f}^{(-)}|$, as follows:

$$[T]_{fi}$$

$$= \langle\bar{\varphi}_{1f}^{(-)}|V_1|\varphi_{0i}\rangle + \langle\varphi_f^{(-)}|H-E|\varphi_i^{(+)}\rangle - \langle\bar{\varphi}_{1f}^{(-)}|H_0+V_1-E|\varphi_i^{(+)}\rangle, \quad (12)$$

where $\langle\bar{\varphi}_{1f}^{(-)}|$ satisfies

$$\langle\bar{\varphi}_{1f}^{(-)}| = \langle\varphi_{0f}| + \langle\bar{\varphi}_{1f}^{(-)}|V_1G_0^{(-)}. \quad (13)$$

The first term in Eq.(12) is the exact T-matrix for the Hamiltonian H_0+V_1.

When we take $|\varphi_i^{(+)}\rangle$ and $\langle\varphi_f^{(-)}|$ as $|\bar{\varphi}_{1i}^{(+)}\rangle$ and $\langle\bar{\varphi}_{1f}^{(-)}|$ respectively, Eq.(12) gives the DWBA result:

$$[T]_{fi} = \langle\bar{\varphi}_{1f}^{(-)}|V_1|\varphi_{0i}\rangle + \langle\bar{\varphi}_{1f}^{(-)}|V-V_1|\bar{\varphi}_{1i}^{(+)}\rangle. \quad (14)$$

In this sense, the expression (12) (or equivalently Eq.(11)) is an extension of DWBA.

C. Unitarity

The variational expression for the S-matrix is given by the following matrix relation:

$$[S] = 1-2\pi i[T]. \tag{15}$$

In general, however, this matrix $[S]$ does not satisfy the unitary condition:

$$SS^{*} = S^{*}S = 1. \tag{16}$$

One way to fulfill Eq.(16) is to formulate the problem in terms of the K-matrix[13], but in that case, we have to use standing waves $\varphi^{(p)}$ instead of $\varphi^{(+)}$ and $\varphi^{(-)}$. One of disadvantages to use standing waves is that we have a difficulty in providing a physically suitable form for $\varphi^{(p)}$. This seems to be very inconvenient for our purpose, because our basic strategy is not to perform any variational procedures, but to use Eq.(11) to evaluate reflection amplitudes with trial functions which become exact in some extreme limit of parameters involved in the Hamiltonian. Another practical difficulty in the k-matrix formalism is that there appears divergent integrals in the formula for an impenetrable potential.

Another way to satisfy Eq.(16) is to 'normalize' $[S]$ by the introduction of $[\tilde{S}]$, defined by

$$[\tilde{S}] = ([S][S^{*}])^{-1/2}[S] \tag{17a}$$

$$= [S]\,([S^{*}][S])^{-1/2}. \tag{17b}$$

For any matrix $[S]$, Eqs.(17a) and (17b) give the same $[\tilde{S}]$. In both

limits of $m/M \to \infty$ and 0, $[\tilde{S}]$ coincides with $[S]$ and there is no problem about the unitarity to leading order in the parameter m M.

D. Reflection amplitudes

Let us apply Eq.(11) to the problem of the Hamiltonian given by Eq.(1'). The normalied free state $|\varphi_{0i}\rangle$ for the incident wave is given by

$$\langle x, y|\varphi_{0i}\rangle = \phi_i^{(0)}(x, y), \tag{18}$$

with

$$\phi_i^{(0)}(x, y) = \sqrt{\mu/2\pi k_i}\exp(-ik_i x)u_i(y), \tag{19}$$

where k_i is related to the total energy E through

$$E = \frac{k_i^2}{2\mu} + i + \frac{1}{2}, \tag{20}$$

and $u_i(y)$ is the eigen function of the harmonic oscillator, given by

$$u_i(y) = (\sqrt{\pi}2^i i!)^{-1/2}H_i(y)\exp(-\frac{1}{2}y^2). \tag{21}$$

Here $H_i(x)$ is an Hermite polynomial. Similarly, the free state for the reflected wave is given by

$$\langle\varphi_{0f}|x, y\rangle = \phi_f^{(0)}(x, y). \tag{22}$$

With these definitions for free states, the reflection amplitude $[R]_{fi}$ is given by

$$[R]_{fi} = [S]_{fi}$$

$$= -2\pi i \int dx \int dy \varphi_f^{(-)*}(x,y)(H-E)\varphi_i^{(+)}(x,y)$$

$$-2\pi i \int dx \int dy \varphi_f^{(-)*}(x,y)(H_0-E)\varphi_i^{(+)}(x,y). \qquad (23)$$

When trial functions $\varphi_i^{(+)}(x,y) \equiv \langle x,y|\varphi_i^{(+)}\rangle$ and $\varphi_f^{(-)*}(x,y) \equiv \langle \varphi_f^{(-)}|x,y\rangle$ satisfy the standard scattering boundary conditions

$$\varphi_i^{(+)}(x,y) \rightarrow \begin{cases} \phi_i^{(0)}(x,y) + \sum_n R_{ni}\phi_n^{(0)}(x,y) & \text{for } x\rightarrow\infty, \\ 0 & \text{for } x\rightarrow-\infty, \end{cases} \qquad (24a)$$

and

$$\varphi_f^{(-)*}(x,y) \rightarrow \begin{cases} \phi_f^{(0)} + \sum_n R_{fn}\phi_n^{(0)}(x,y) & \text{for } x\rightarrow\infty, \\ 0 & \text{for } x\rightarrow-\infty \end{cases} \qquad (24b)$$

Eq.(23) can be reduced to

$$[R]_{fi} = R_{fi} - 2\pi i \int dx \int dy \varphi_f^{(-)*}(x,y)(H-E)\varphi_i^{(+)}(x,y). \qquad (25)$$

This is just an expression in the standard variational approach.[10,11] Therefore an extension of the standard variational

method is made in Eq.(23) in which the second integral replaces the requirement of the conditions (24a) and (24b) for trial functions.

III. Approach from Adiabatic Regime

In this section, we evaluate $[R]_{f_1}$ in Eq.(23) with trial functions which become exact in the limit of $\mu \gg 1$ in the Hamiltonian (1'). When μ becomes very large, we can neglect the kinetic energy term of incidon in zeroth-order approximation. Then the equation to determine the motion of oscillator can be written as

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}y^2 + V(x-y)\right]Y_n(y;x) = V_n(x)Y_n(y;x), \tag{26}$$

where the boundary conditions for the normalized wave function $Y_n(y;x)$ are given by

$$Y_n(y;x) \to 0 \text{ as } y \to \pm\infty. \tag{27}$$

In Eq.(26), x is an 'external' parameter and the eigenvalue $V_n(x)$ provides and 'adiabatic potential' for the incidon. Namely, the motion of incidon is determined by

$$\left[-\frac{1}{2\mu}\frac{d^2}{dx^2} + V_n(x)\right]X_n(x) = EX_n(x), \tag{28}$$

with the following boundary conditions:

$$X_n(x) \rightarrow \begin{cases} \sqrt{\mu/2\pi k_n}\, e^{-ik_n x} + \sqrt{\mu/2\pi k_n}\, e^{ik_n x + i\delta_n} & \text{for } x \rightarrow \infty, \\ 0 & \text{for } x \rightarrow -\infty, \end{cases} \tag{29}$$

where δ_n is the phase shift to be determined by the solution of the Schrödinger equation (28). Clearly, as $x \rightarrow \infty$, $Y_n(x;x)$ and $Y_n(y;x)$ approach $n+1/2$ and $u_n(y)$ respectively. Thus k_n is determined by the relation

$$E = \frac{k_n^2}{2\mu} + n + \frac{1}{2}. \tag{30}$$

By multiplying X_n by Y_n, we obtain a trial wave function as

$$\varphi_n{}^{(-)}(x,y) = \varphi_n{}^{(-)*}(x,y) = \varphi_n{}^{(adi)} \equiv X_n(x)Y_n(y;x), \tag{31}$$

which becomes exact in the limit $\mu \rightarrow \infty$ and is expected to be still a good trial function for $\mu >> 1$. The wave funcetion $\varphi_n{}^{(adi)}$ has a property of only an elastic reflection with the amplitude $\exp(i\delta_n)$.

The inelastic reflection amplitudes can be evaluated with the use of Eq.(23) (or rather Eq.(25) in this case) and the trial function (31). The result is given by

$$[R]_{fi} = e^{i\delta_i}\delta_{fi}$$

$$- \frac{2\pi i}{\mu} \int dx \int dy \left\{ \frac{\partial Y_i(y;x)}{\partial x} Y_f(y;x) \left[-X_i'(x)X_f(x) + X_i(x)X_f'(x) \right] \right.$$

$$+ \frac{\partial Y_i(y;x)}{\partial x} \frac{\partial Y_f(y;x)}{\partial x} X_i(x) X_f(x) \Big\}, \tag{32}$$

where δ_{fi} is the Kronecker's delta function. Equation (32) shows that 'non-adiabatic' transitions occur only when $\partial Y_n(y;x)/\partial x$ does not vanish.

In Fig.1, we have shown the numerical results of transition probabilities $|[R]_{f0}|^2$ and the normalized ones $|[\tilde{R}]_{f0}|^2$ for the case of the hard-core potential and μ=5. Solid curves represent the exact results, given by Secrest and Johnson[15], while the broken and dotted ones show the results of $|[\tilde{R}]_{f0}|^2$ and $|[R]_{f0}|^2$ respectively. We have also calculated the case of μ=0.5, but the results for both $|[R]_{fi}|^2$ and $|[\tilde{R}]_{fi}|^2$ are not good except near the threshold, namely

$$E \sim \max\{i + \frac{1}{2}, f + \frac{1}{2}\}, \tag{33}$$

at which the motion of the incidon is always very slow irrespective of μ.

IV. Approach from Anti-Adiabatic Regime

When μ is very small, the kinetic energy term in the Hamiltonian (1') becomes very important and the free motion of oscillator can be neglected in zeroth-order approximation. However, we cannot neglect the potential term $V(x-y)$, because this is always larger than the kinetic energy for an impenetrable

potential. Thus in zeroth-order approximation, we should consider the following equation first:

$$[-\frac{1}{2\mu}\frac{\partial^2}{\partial x^2} + V(x-y)]\,\tilde{X}_n(x;y) = \frac{k_n^2}{2\mu}\,\tilde{X}_n(x;y), \tag{34}$$

with the boundary conditions for $\tilde{X}_n$ as

$$\tilde{X}_n(x;y) \to \begin{cases} \sqrt{\mu/2\pi k_n}\; e^{-ik_n x} + \sqrt{\mu/2\pi k_n}\, e^{ik_n x + i\delta_n} & \text{for } x\to\infty, \\ 0 & \text{for } x\to-\infty. \end{cases} \tag{35}$$

It should be noted that the phase shift δ_n will depend on y, in contrast with the case of Eq.(29). By considering the difference between $\tilde{X}_n(x;y)$ and $\tilde{X}_n(x;0)$, we can write $\tilde{X}_n(x;y)$ in terms of $\tilde{X}_n(X) \equiv \tilde{X}_n(x;0)$ as

$$\tilde{X}_n(x;y) = e^{-ik_n y}\tilde{X}_n(x-y). \tag{36}$$

The motion of oscillator can be determined in zeroth-order approximation as

$$(-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}y^2)\tilde{Y}_n(y) = (n+\frac{1}{2})\tilde{Y}_n(y). \tag{37}$$

This is nothing but the equation for a free harmonic oscillator and the solution is $u_n(y)$. Combining $X_n(x;y)$ with $u_n(y)$, we obtain a trial wave function as

$$\varphi_n^{(-)}(x,y) = \varphi_n^{(-)*}(x,y) = \varphi_n^{(anti)}(x,y) \equiv u_n(y)\,e^{-ik_n y}\tilde{X}_n(x-y), \tag{38}$$

which becomes exact in the limit $\mu \to 0$.

Since the trial wave function (38) does not satisfy the standard scattering boundary conditions (24), we have to use Eq.(23) to calculate $[R]_{fi}$. The result is

$$[R]_{fi} = \{-2\pi i \int dx\ V(x)\tilde{X}_f(x)\tilde{X}_i(x)$$

$$- 2\pi i \frac{1+\mu}{2\mu} \int dx [\tilde{X}'_f(x) + ik_f \tilde{X}_f(x)]\ [\tilde{X}'_i(x) + ik_i \tilde{X}_i(x)]\}$$

$$\times \int dy\ u_f(y) u_i(y) \exp\ [-i(k_i + k_f)y]. \tag{39}$$

In deriving Eq.(39), we have used the relations

$$\int dy\ u_n(y) u_m(y) e^{-iay} = \sqrt{2^m m!/2^n n!}\,(-ia)^{n-m} e^{-a^2/4} L_m^{(n-m)}\left(\frac{a^2}{2}\right), \tag{40}$$

and

$$\int dy\ u_n(y)\ \frac{du_m(y)}{dy} e^{-iay} = i\left(\frac{a}{2} - \frac{n-m}{a}\right) \int dy\ u_n(y) u_m(y) e^{-iay}, \tag{41}$$

where $L_m^{(\alpha)}(x)$ is the associated Laguerre polynomial, defined by

$$L_m^{(\alpha)}(x) = \frac{e^x x^{-\alpha}}{m!}\ \frac{d^m}{dx^m}(e^{-x} x^{m+\alpha}). \tag{42}$$

In the following, we will evaluate Eq.(39) for several types of potentials.

A. Hard-core potential

When $V(x)=V_{HC}(x)$, $\tilde{X}_n(x)$ is easily solved to be

$$\tilde{X}_n(x) = \sqrt{\mu/2\pi k_n}(e^{-ik_n x} - e^{ik_n x})\theta(x). \tag{43}$$

Thus we obtain

$$[R]_{fi} = -2\frac{\sqrt{k_i k_f}}{k_i+k_f}(1+\mu)\int dy\ u_f(y)u_i(y)\ \exp\ [-i(k_i+k_f)y]. \tag{44}$$

As μ approaches zero with the total energy E fixed, k_n also approaches zero. Therefore, Eq.(44) has the following expansion in terms of μ:

$$[R]_{fi} = -\delta_{fi}+2i\sqrt{k_i k_f}\int dy\ u_f(y)u_i(y)y. \tag{45}$$

This agrees with the exact result obtained by other methods.[6,21,22] The elastic term becomes dominant, while the inelastic terms involve only one quantum jumps to leading order of μ whose amplitudes are proportional to $\sqrt{\mu}$.

In Fig.2, we have shown the results for transition probabilities $|[R]_{f0}|^2$ and the normalized ones $|[\tilde{R}]_{f0}|^2$ for the cases of (a) μ=0.125 and (b) μ=0.5, together with the exact results of Secrest and Johnson.[15] (Solid, dotted, and broken curves correspond, respectively, to the exact results, $|[R]_{f0}|^2$, and $|[\tilde{R}]_{f0}|^2$.) The agreement between $|[\tilde{R}]_{f0}|^2$ and the exact results is excellent for all calculated energies E for the case of μ=0.125. Even for μ=0.5, the qualitative features are reproduced in our calculation of $|[\tilde{R}]_{f0}|^2$.

B. Soft-core potential

We can solve $\tilde{X}_n(x)$ with the use of the modified Bessel function $K_\mu(z)$ for the soft-core potential $V_{sc}(x)$. The result is

$$\tilde{X}_n(x) = -i\sqrt{\mu/2\pi k_n}\cdot\frac{4k_n}{\alpha}\cdot\frac{(2\mu/\alpha^2)^{-ik_n/\alpha}}{\Gamma(1-i2k_n/\alpha)}\,K_{i2k_n/\alpha}(\sqrt{8\mu/\alpha^2}\,e^{-\alpha x/2}), \qquad (46)$$

where $\Gamma(x)$ is the gamma function. We can perform the integrals in Eq.(39) and obtain

$$[R]_{fi} = -\frac{2\sqrt{k_i k_f}}{k_i+k_f}(1+\mu)\left(1+i\frac{\mu}{1+\mu}\,\frac{k_i+k_f}{\alpha}\right)$$

$$\times\left(\frac{2\mu}{\alpha^2}\right)^{-i(k_i+k_f)/\alpha}\frac{|\Gamma(1+i(k_i+k_f)/\alpha)|^2\;|\Gamma(1+i(k_i-k_f)/\alpha)|^2}{\Gamma(1-i2k_i/\alpha)\;\Gamma(1-i\;2k_f/\alpha)}$$

$$\times\int dy\;\; u_f(y)u_i(y)e^{-i(k_i+k_f)y}. \qquad (47)$$

As μ approaches zero, Eq.(47) has the same asymptotic behavior as given in Eq.(45). Namely, there is no difference between the hard- and soft-core potentials in the limit $\mu\to 0$. The same asymptotic behavior is also expected for any potential $V(x)$ *which becomes infinite at some point* x_0 *and goes to zero* sufficiently quickly for $x\to\infty$. (The type of potentials considered here is illustrated in Fig.3.) This can be seen rather easily by evaluating the leading correction term in the difference of reflection amplitude, $\Delta[R]_{fi}$, between $V(x)$ and $V_{HC}(x-x_0)$. We have

$$\Delta[R]_{fi} = -2\pi i \int_{-\infty}^{\infty} dx [V(x+x_0) - V_{HC}(x)]$$

$$\times [\tilde{X}_f(x)\tilde{X}_i(x) + (1+\mu)e^{-ik_i x}\tilde{X}_i(x)\int_x^{\infty} dt \{\frac{d\tilde{X}_f(t)}{dt} + ik_f\tilde{X}_f(t)\}e^{ik_f t}$$

$$+ (1+\mu)e^{-ik_f x}\tilde{X}_f(x)\int_x^{\infty} dt \{\frac{d\tilde{X}_i(t)}{dt} + ik_i\tilde{X}_i(t)\}e^{ik_i t}]$$

$$\times \int dy\ u_f(y)u_i(y)e^{-i(k_i+k_f)y}, \qquad (48)$$

where $\tilde{X}_n(t)$ is given in Eq.(43). As μ goes to zero, Eq. 48) has the following form:

$$\Delta[R]_{fi} = -4\mu\frac{\sqrt{k_i k_f}}{k_i+k_f}\int dx\ [V(x+x_0) - V_{HC}(x)]x$$

$$\times \int dy\ u_f(y)\ u_i(y)\ e^{-i(k_i+k_f)y}. \qquad (49)$$

Thus $\Delta[R]_{fi}$ is at most of the order of μ and is negligible. Physically, such a general behavior stems from the fact that as μ approaches zero, the de Broglie wavelength of incidon becomes so long that the incidon cannot see details of the potential.

When we treat the case of finite μ and small α, Eq. 47) will give much different results from those of Eq.(44). In order to check this situation, we have plotted $|[\tilde{R}]_{10}|^2$ in Fig.4 for the cases (a) α=4 and (b) α=0.7 and compared with the exact resutls of Secrest and Johnson[15] and those in DWBA. (To calculate the results in DWBA, we have used Eq.(14) with $V_1(z)=V(x)$ and

$$\bar{\varphi}_{1n}^{(+)}(x,y) = \bar{\varphi}_{1n}^{(-)*}(x,y) - \varphi_n^{(DWBA)}(x,y) = u_n(y)\tilde{X}_n(x), \qquad (50)$$

where $\tilde{X}_n(x)$ is given in Eq.(46).) Solid, broken, and dotted curves correspond, respectively, to the exact results, $|[\tilde{R}]_{10}|^2$ calculated with the use of Eqs.(17) and (47), and the results in DWBA. The mass ratio μ is taken to be 0.5. For large α, Eq.(47) gives essentially the same results as Eq.(44) and provides a rather good description, while DWBA gives quite poor results. The opposite is true for small α. Physically, the heavy oscillator will not change its motion appreciably by an impulsive collision with a light particle. This is the reason for the success of Eq.(44) for the hard-core potential. However, as the "interaction time" becomes longer than ω^{-1}, which can occur for the very soft potential, we have to consider effects on the motion of oscillator. In the trial function (38), those effects are not taken into account.

C. Step-function potential

The step-function potential $V_0\theta(-x+y)$ gives a little different behavior for $[R]_{f_1}$ in the limit $\mu \to 0$. The wave function $\tilde{X}_n(x)$ is given by

$$\tilde{X}_n(x) = \sqrt{\mu/2\pi k_n}\,\{\theta(x)\,[e^{-ik_n x} + R_n e^{ik_n x}]$$

$$+ \theta(-x)(1-R_n)e^{k_n x}\}, \qquad (51)$$

where

$$R_n = \frac{ik_n+\kappa_n}{ik_n-\kappa_n}, \tag{52}$$

and

$$\kappa_n = \sqrt{2\mu(V_0-E+n+1/2)} \quad . \tag{53}$$

As μ approaches zero, $[R]_{fi}$ has the following form:

$$[R]_{fi} = R_i\delta_{fi} - i\mu\frac{V_0}{\sqrt{k_i k_f}}(1+R_i)(1+R_f)\int dy\ u_f(y)u_i(y)y. \tag{54}$$

Qualitatively, Eq.(54) indicates the same results as Eq.(45). In addition, when V_0 becomes infinite, Eq.(54) is reduced to Eq.(45).

The same asymptotic behavior of Eq.(54) is expected for a potential having the form illustrated in Fig.5 in which the point x_0 is determined by the following relation:

$$\int_{-\infty}^{\infty} dx\ [V(x) - V_0\theta(-x+x_0)] = 0. \tag{55}$$

The proof of the above statement goes in a similar way as in Sec.IV.B. The difference $\Delta[R]_{fi}$ is given by Eq.(48) in which V_{HC} is replaced by $V_0\theta(-x)$ and $\tilde{X}_n$ is defined in Eq.(51). Thus, as μ approaches zero, the leading correction terms for $\Delta[R]_{fi}$ is given as follows:

$$\Delta[R]_{fi} = \frac{\mu}{\sqrt{k_i k_f}}\int_{-\infty}^{\infty} dx\ [V(x+x_0) - V_0\theta(-x)]x$$

$$\times \{k_i(1-R_i)R_f \frac{2k_f}{k_i+k_f} + k_f(1-R_f - R_i\frac{2k_i}{k_i+k_f}$$

$$- k_f(1-R_f)(1+R_i) - k_i(1-R_i)(1-R_f)\}$$

$$\times \int dy\ u_f(y)u_i(y)e^{-i(k_i-k_f)y} \quad . \tag{56}$$

In deriving Eq.(56), Eq.(55) is used. As in the previous subsection, $\Delta[R]_{fi}$ is at most of the order of μ and is negligible compared with the terms in Eq.(54).

V. Discussion

We have applied a variational expression (Eq.(11)) to collisions of a particle with a harmonic oscillator in one dimension. We have used trial functions $\varphi_n^{(adi)}(x,y)$ (Eq.(31)) and $\varphi_n^{(anti)}(x,y)$ (Eq.(38)) in the expression to obtain exact results in the limits $\mu\to\infty$ and $\mu\to 0$, where μ is the mass ratio m/M. In particular, we have derived exact expressions for inelastic as well as elastic collisions to leading order in the parameter μ for any impenetrable interaction potential in the limit $\mu\to 0$.

For finite μ, we have obtained a rather accurate formula (Eq.(44)) for the reflection amplitudes, when μ is smaller than unity and the interaction is a hard-core type potential. However, for a soft-core potential and the case of $\mu\sim 1$, Eq.(44) gives poorer results than DWBA. We can improve on our results by introducing some variational parameters in our trial functions and determining them by a variational procedure. One possible

way is to give the trial function in the following way:

$$\varphi_n(x,y) = \lambda\varphi_n^{(adi)}(x,y) + (1-\lambda)\varphi_n^{(anti)}(x,y), \tag{57}$$

where λ is a variational parameter. This is the combination of the adiabatic and anti-adiabatic approaches. Another way is to give

$$\varphi_n(x,y) = u_n(y)e^{-i\lambda k_n y}\tilde{X}_n(x-\lambda y), \tag{58}$$

where $\tilde{X}_n(x) \equiv \tilde{X}_n(x;y=0)$ is defined in Eqs.(34) and (35). When $\lambda=1$, $\varphi_n(x,y)$ is reduced to $\varphi_n^{(anti)}(x,y)$ while for $\lambda=0$, $\varphi_n(x,y)$ is nothing but $\varphi_n^{(DWBA)}(x,y)$ defined in Eq.(50). Thus this is the combination of the anti-adiabatic approach with DWBA.

In the near future, we will extend our method to treat collisions in three dimension, in particular, gas-surfacde scattering problems.

Acknowledgment

The author would like to thank Professor W. Kohn for suggesting this work, for stimulating discussions, and for a critical reading of the manuscript. He also wishes to thank Professor R.E. Peierls for useful communication. The author is grateful to the support of the National Science Foundation (Grant DMR 8703434) and the office of Naval Research (Contract N00014-84-K-0548).

References

* Present address.

1. For a review, see, for example, V. Celli, in *Many-Body-Phenomena at Surfaces*, edited by D. Langreth and H. Suhl (Academic, Orlando, 1984), p.315 and references therein.
2. J.C. Tully, J. Chem. Phys. 73, 1975 (1980); in *Many-Body-Phenomena at Surfaces*, edited by D. Langreth and H. Suhl (Academic, Orlando, 1984), p.377.
3. A.C. Levi, Nuovo Cimento 54B, 357 (1979).
4. W. Brenig, Z. Phys. B36, 81 (1979); D.M. Newns, in *Dynamical Processes and Ordeing on Solid Surfaces*, edited by A. Yoshimori and M. Tsukada (Springer, Berlin, 1985), p.26.
5. E.J. Heller, J. Chem. Phys. 62, 1544 (1975); S. Sawada, R. Heather, B. Jackson, and H. Metiu, J. Chem. Phys. 83, 3009 (1985).
6. J.M. Jackson and N.F. Mott, Proc. Roy. Soc. (London) A 137, 703 (1932).
7. J.E. Lennard-Jones and C. Strachan, Proc. Roy. Soc. (London) A 150, 442 (1935).
8. There are many papers on DWBA, for example, N. Cabrera, V. Celli, F.O. Goodman, and R. Manson, Surf. Sci. 19, 67 (1970). Most recent paper is :D. Eichenauer and J.P. Toennnies, J. Chem. Phys. 85, 532 (1986).
9. Recently, a time-dependent variational approach was proposed

by M.A.M. de Aguiar and C.P. Malta (J. Chem. Phys. 84, 6916 (1986)), but both their intent and method are much different from us. Their approach is very close to the semiclassical gaussian basis set method.

10. L. Hulthén, K. Fysiogr. Saellsk. Lund, Foerh. 14, 21 (1944); Ark. Mat. Astron. Fys. 35A, 25 (1948).
11. W. Kohn, Phys. Rev. 74, 1763 (1948).
12. J.M. Blatt and J.D. Jackson, Phys. Rev. 76, 18 (1949).
13. K. Takatsuka and V. Mckoy, Phys. Rev. Lett. 45, 1396 (1980); Phys. Rev. A23, 2352, 2359 (1981).
14. E.K.U. Gross and E. Runge, Phys. Rev. A26, 3004 (1982).
15. D. Secrest and B.R. Johnson, J. Chem. Phys. 45, 4556 (1966).
16. J.D. Kelley and M. Wolfsberg, J. Chem. Phys. 44, 324 (1966).
17. P. Pechukas, Phys. Rev. 181, 166, 174 (1969).
18. A.P. Penner and R. Wallace, Phys. Rev. A7, 1007 (1973); A9, 1136 (1974).
19. W.H. Miller, J. Chem. Phys. 53, 1949, 3578 (1970); in *Advances in Chemical Physics* (Wiley, New York, 1974), vol.25, p.69.
20. W.H. Miller and T.F. George, J. Chem. Phys. 56, 5668 (1972); J. Stine and R.A. Marcus, Chem. Phys. Lett. 15, 536 (1972).
21. B. Widom, J. Chem. Phys. 30, 238 (1959).
22. R.E. Peierls, private communication.

Figure Captions

Fig. 1. Transition probabilities for a harmonic oscillator interacting with a particle as a function of total energy E. The hard-core potential is assumed. The mass ratio μ is 5. Solid, dotted, and broken curves represent, respectively, the exact results of Secrest and Johnson, $|[R]_{f0}|^2$ given by Eq.(32), and $|[\tilde{R}]_{f0}|^2$ given by Eq.(17) with the use of those $[R]_{f0}$.

Fig. 2. Transition probabilities for a harmonic oscillator interacting with a particle as a function of total energy E. The mass ratios μ are 0.125 and 0.5 in (a) and (b), respectively. As in Fig.1, the hard-core potential is assumed. The exact results of Secrest and Johnson are shown by a solid curve, while $|[R]_{f0}|^2$ given by Eq.(44), and normalized ones $|[\tilde{R}]_{f0}|^2$, given by Eq.(17) with the use of those $[R]_{f0}$, are plotted by dotted and broken curves, respectively.

Fig. 3. A type of potential which gives the reflection amplitudes in the form of Eq.(45) as μ approaches zero.

Fig. 4. Transition probabilities for the soft-core potential case. The mass ratio μ is taken to be 0.5. Solid, broken, and dotted curves correspond, respectively, to the exact results of Secrest and Johnson, $|[\tilde{R}]_{10}|^2$ with the use of Eq.(17) and (47), and those in DWBA. Cases of α=4 and α=0.7 are treated in (a) and (b), respectively.

Fig. 5. A type of potential which gives the reflection amplitudes in the form of Eq.(54) in the limit $\mu \to 0$.

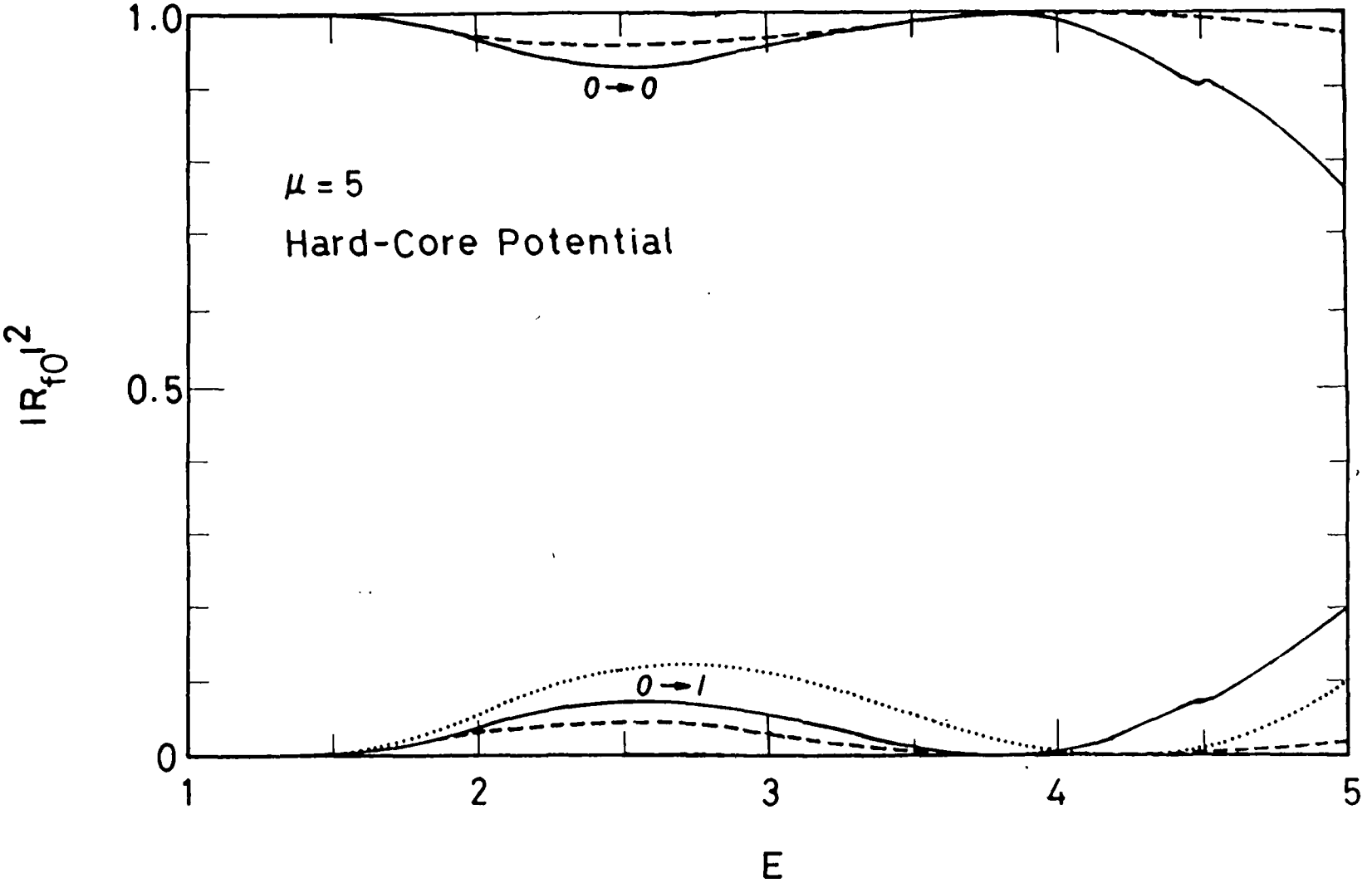


Fig 1 Y Takada Phys Rev B15

(a)

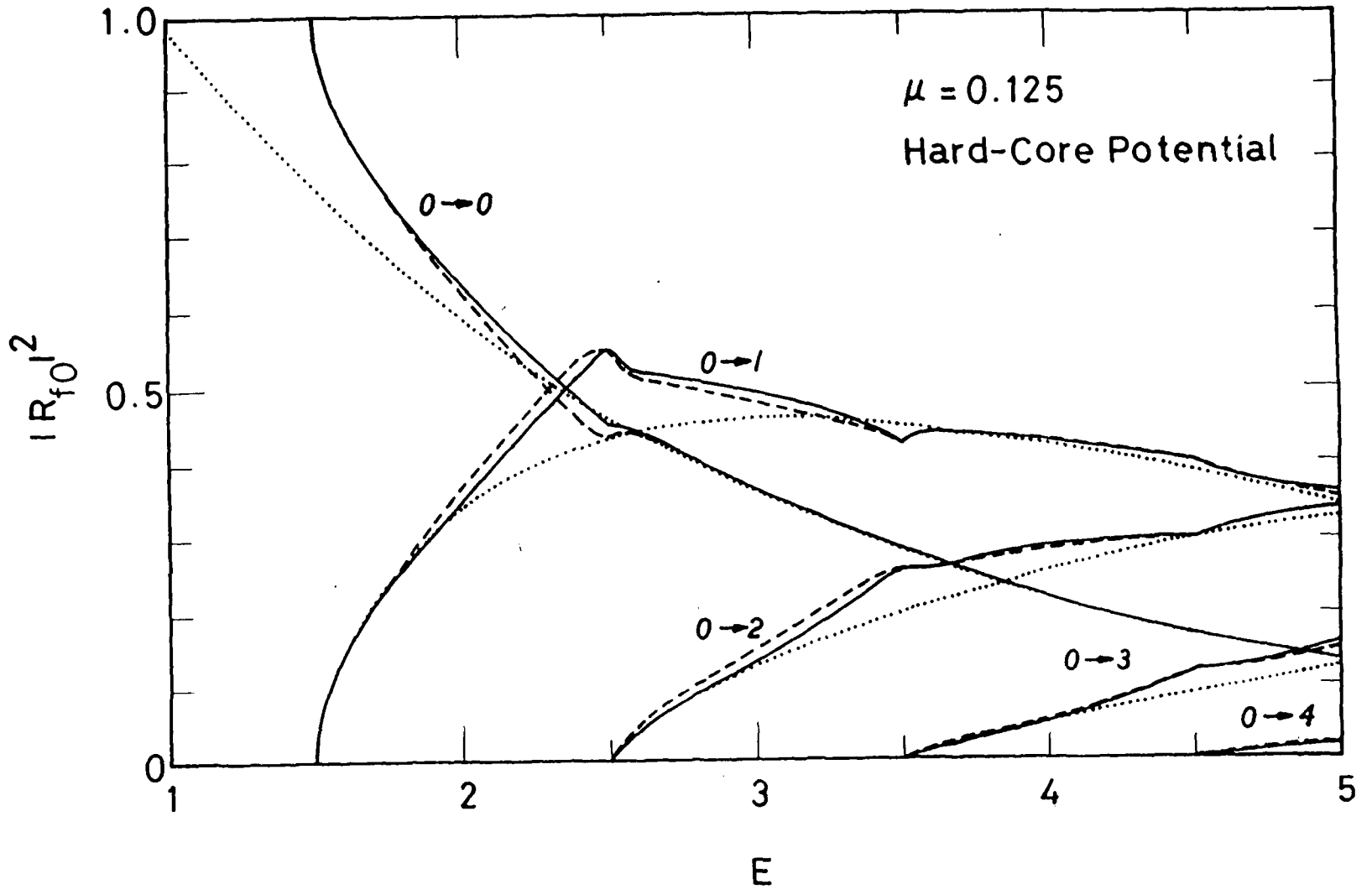


Fig 2 (a) Y. Takeda Phys Rev B15

(b)

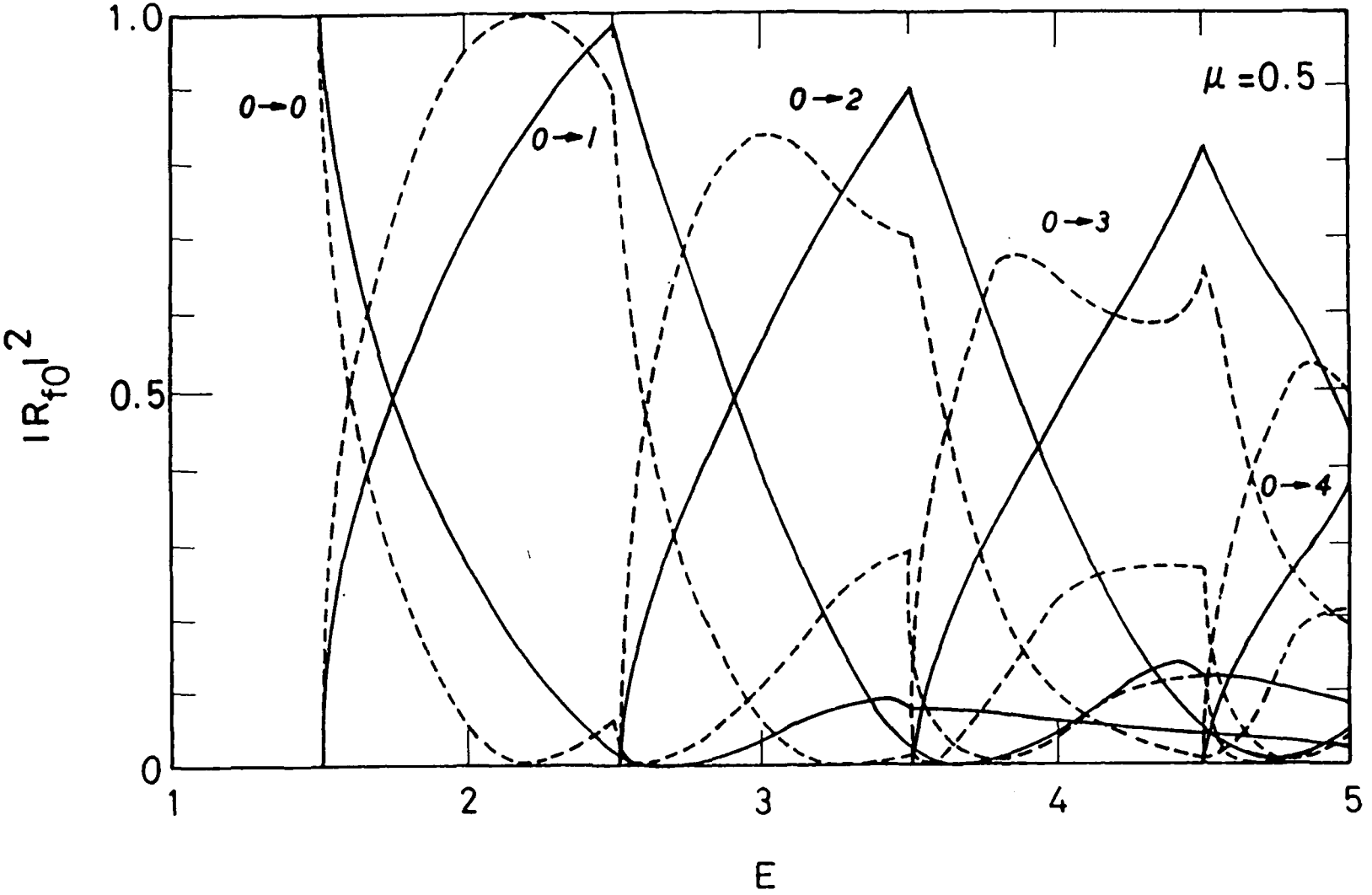


Fig 2(b) " Talcada Phys Rev B15

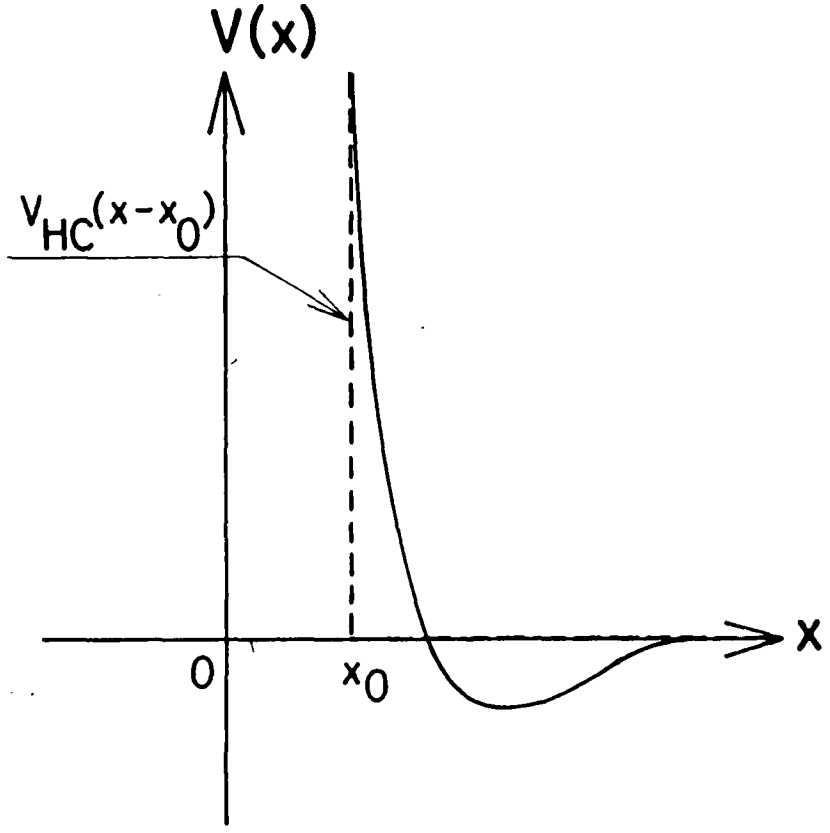
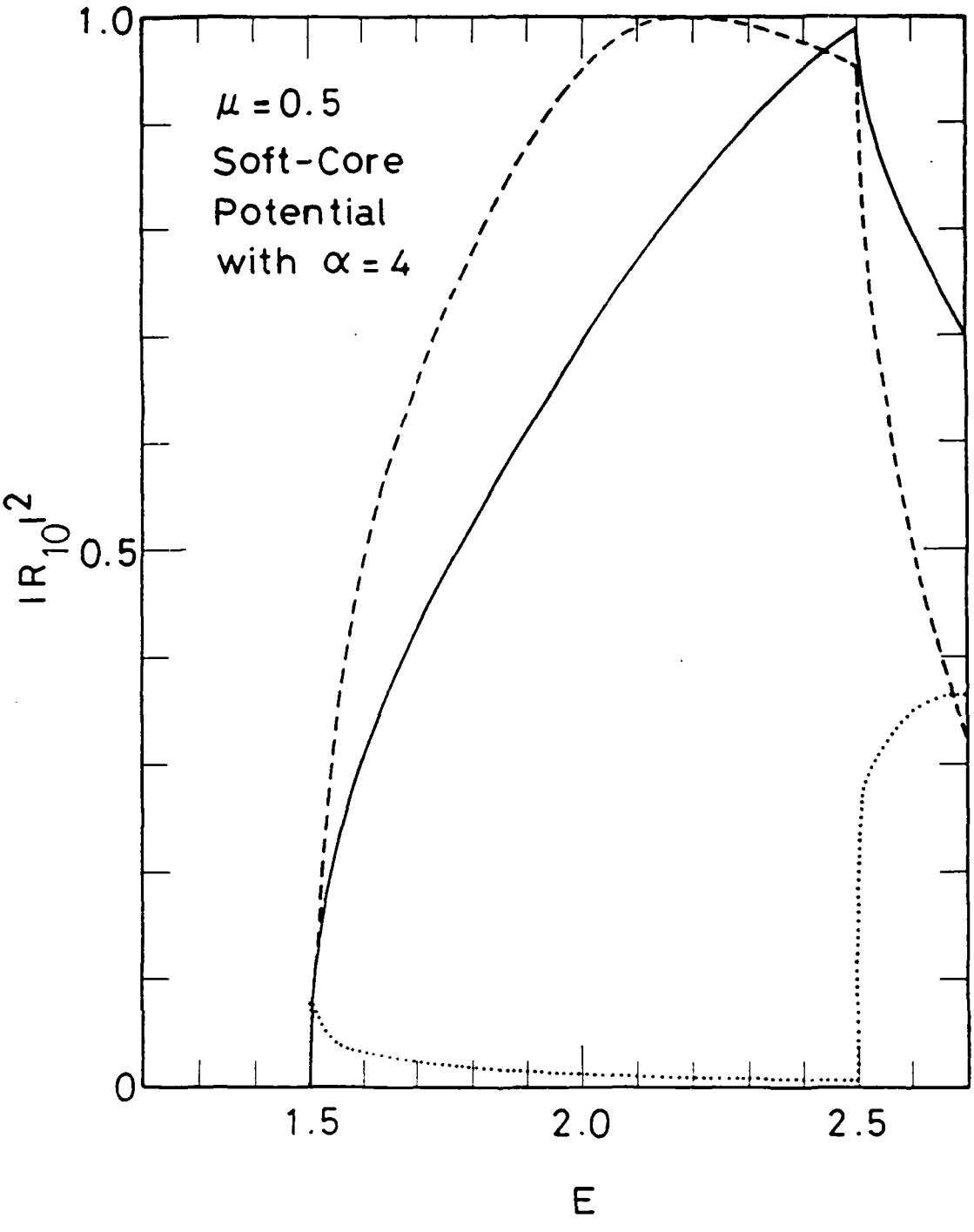


Fig 3. Y. Takeda Phys. Rev B15

(a)



(b)

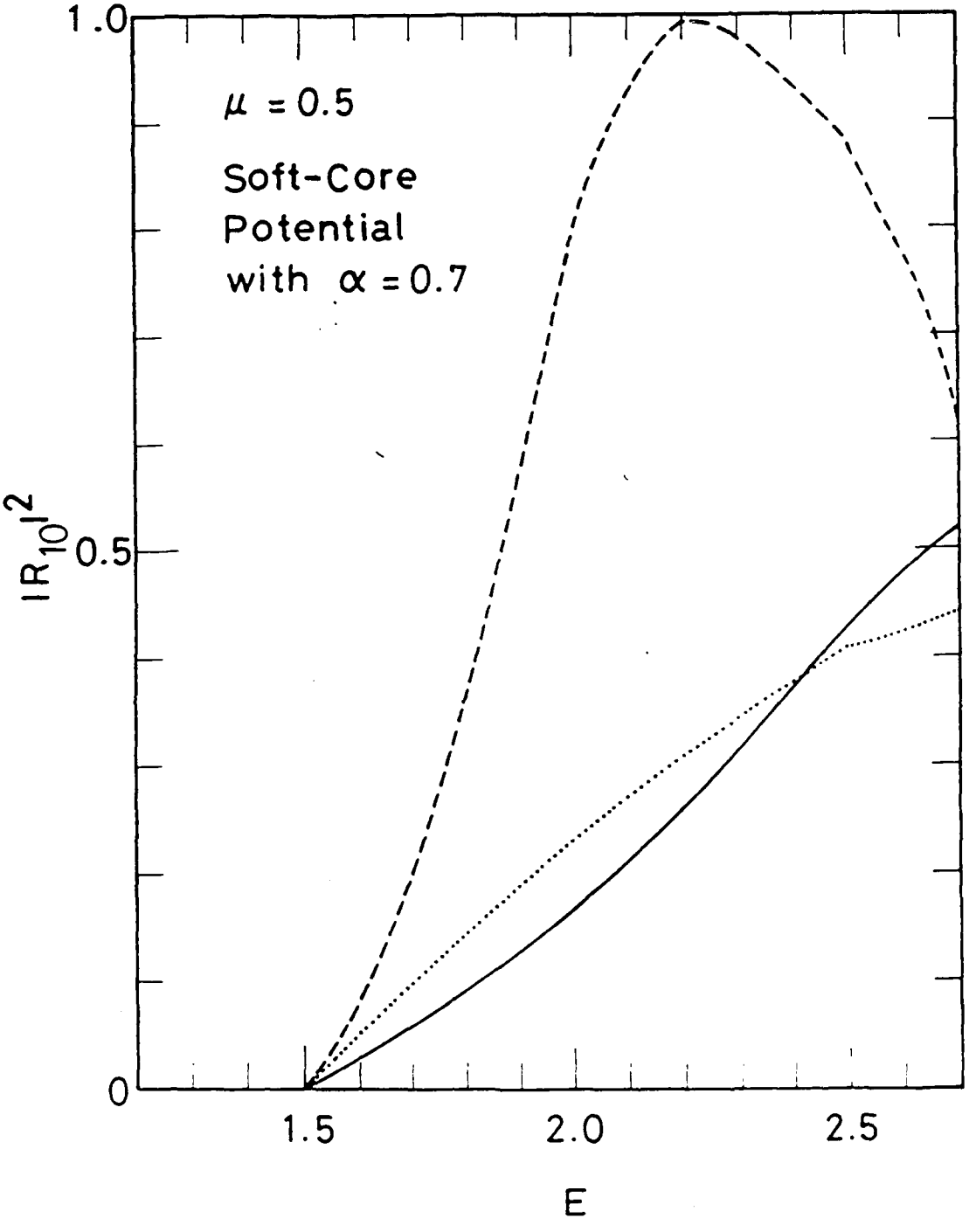


Fig 4(b) T. Takeuda Phys. Rev 1973

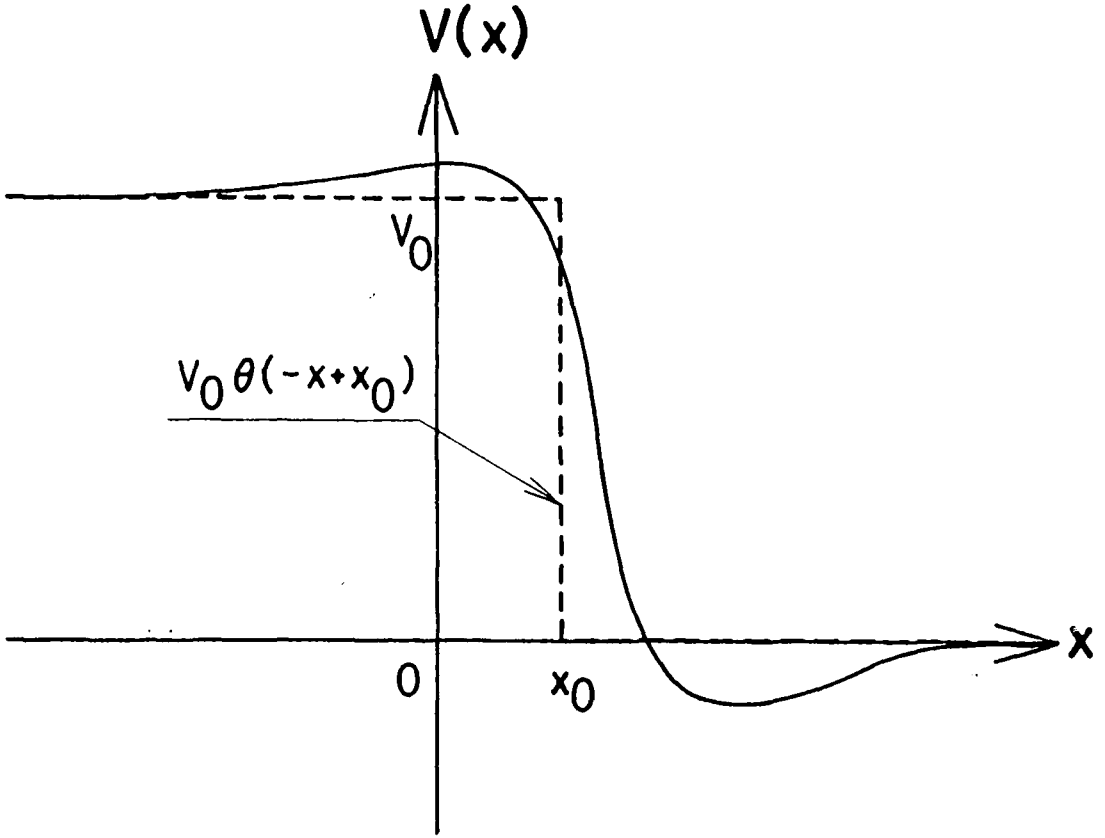


Fig. 5 Y. Takada Phys Rev B 15